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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : C08F 8/20 — A1

(11) International Publication Number: WO 86/ 03499

(43) International Publication Date: 19 June 1986 (19.06.86)

(21) International Application Number: PCT/US85/02329

(22) International Filing Date: 26 November 1985 (26.11.85)

(31) Priority Application Number: 678,442

(32) Priority Date: 5 December 1984 (05.12.84)

(33) Priority Country: US

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(81) Designated States: AU, BE (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, NL (European patent), SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: HALOGENATED ETHYLENE POLYMERS WITH IMPROVED RESISTANCE TO AGGLOMERATION

(57) Abstract

Halogenated polyethylene resins and halogenated ethylene polymer resins having a reduced tendency to 'block'. The halogenated resins are prepared respectively from polyethylene and ethylene polymer starting materials which have a weight-based median particle size of from 160 to 600 microns and a weight-based particle size distribution such that more than 60 percent of the particles have a particle size of from 150 to 850 microns. The halogenated resins also have a weight-based median particle size of from 200 to 900 microns. The halogenated polyethylene resins have a chemically combined halogen content of from 26 to 42 weight percent whereas the halogenated ethylene polymer resins have a chemically combined halogen content of from 15 to 28 weight percent. The halogenated ethylene polymer resins are prepared from ethylene polymer starting materials which have polymerized therein up to five weight percent of 1-olefin monomer copolymerizable with ethylene.

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HALOGENATED ETHYLENE POLYMERS WITH IMPROVED RESISTANCE TO AGGLOMERATION

The present invention relates to halogenated polyethylene and halogenated ethylene interpolymer resins which are resistant to aggolmeration. More particularly, the present invention relates to agglomeration-resistant chlorinated ethylene homopolymer resins and chlorinated ethylene polymer resins.

"Blocking" is a term used to define the tendency of a polymeric resinous powder to form clumps or lumps by agglomeration. Blocking is undesirable because users of resinous powders want free-flowing powders for blending purposes. Resinous powders which block during storage or transport thereof require additional handling to break up agglomerates if blocking is not unacceptably high. Resinous powders with excessively high blocking are of little value because they tend to fuse into a solid mass. In other words, as blocking decreases, desirability and practical utility increase.

In one aspect, the present invention is a halogenated derivative of polyethylene which is resistant to agglomeration or blocking. The halogenated polyethylene has three definitive physical properties. First, it has a neat wedge blocking value of from zero to 60 kilograms. Second, it has a weight-based median particle size of from 200 to 900 microns. Third, it has a chemically combined halogen content of from 26 to 42 percent by weight of derivative.

The halogenated polyethylene is prepared from a polyethylene resin having four characteristic physical properties. First, the resin has a weight-based median particle size of from 160 to 600 microns. Second, it has a weight-based particle size distribution wherein more than 60 percent by weight of the particles have a particle size of from 150 to 850 microns. Third, it has a bulk density of from 0.26 to 0.56 grams per cubic centimeter. Finally, it has a density of from 0.958 to 0.965 grams per cubic centimeter.

In a second aspect, the present invention is a halogenated derivative of an ethylene polymer which is resistant to agglomeration or blocking. The derivative has four definitive physical properties. First, it has a neat wedge blocking value of from zero to 60 kilograms. Second, it has a weight-based median particle size of from 200 to 900 microns. Third, it has a chemically combined halogen content of from 15 to 28 percent by weight of derivative. Fourth, it has a heat of fusion of from zero to three calories per gram.

The derivative is prepared from an ethylene polymer resin which has polymerized therein from 95 to 99 weight percent ethylene and from five to one weight percent of 1-olefin monomer copolymerizable therewith, both percentages being based on polymer weight. More than one 1-olefin monomer may be polymerized with ethylene provided the total amount of 1-olefin monomer does not exceed five weight percent.

The ethylene polymer has four characteristic physical properties. First, the polymer has a weight-based median particle size of from 160 to 600 microns. Second, it has a weight-based particle size distribution wherein more than 60 percent by weight of the particles have a particle size of from 150 to 850 microns. Third, it has a bulk density of from 0.25 to 0.60 grams per cubic centimeter. Finally, it has a density of from 0.935 to 0.950 grams per cubic centimeter.

As used herein, the term "polyethylene" means homopolymers of ethylene. Polyethylene resins suitable for purposes of the present invention desirably meet four criteria.

One criterion is a weight-based median particle size of from 160 to 600 microns. The median particle size is beneficially from 160 to 450 microns. As used herein, the term "weight-based median particle size" means a particle size above and below which there is, in a sieve analysis of a resin sample, an equal weight of resin.

A second criterion is a weight-based particle size distribution in which more than 60 percent by weight of the particles have a size of from 150 to 850 microns. Beneficially, more than 60 percent by weight of the particles have a size of from 150 to 500 microns. Desirably, more than 60 percent by weight of the particles have a size of from 150 to 425 microns.

A third criterion is a bulk density of from 0.26 to 0.56 grams per cubic centimeter. A fourth criterion is a density of from 0.958 to 0.965 grams per cubic centimeter.

As used herein, the term "ethylene polymer" means interpolymers of ethylene having polymerized therein ethylene and a total amount of 1-olefin monomer copolymerizable therewith. The total amount is suitably from 1 to 5 percent by weight of interpolymer. The total amount of 1-olefin monomer is beneficially from 1.2 to 3.5 percent by weight of interpolymer. More than one 1-olefin monomer may comprise the total amount. Suitable 1-olefin monomers include 1-butene and 1-octene. Ethylene polymer resins suitable for purposes of the present invention desirably meet four criteria.

One criterion for ethylene polymer resins is a weight-based median particle size of from 160 to 600 microns. The median particle size is beneficially from 160 to 450 microns.

A second criterion is a weight-based particle size distribution in which more than 60 percent by weight of the particles have a size of from 150 to 850

microns. Beneficially, more than 60 percent by weight of the particles have a size of from 150 to 500 microns. Desirably, more than 60 percent by weight of the particles have a size of from 150 to 425.

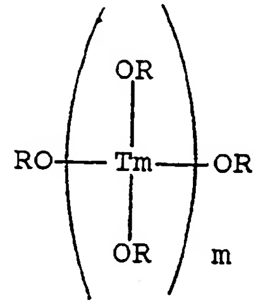
A third criterion is a bulk density of from 0.25 to 0.60 grams per cubic centimeter. A fourth criterion is a density of from 0.935 to 0.950 grams per cubic centimeter.

Polyethylene resins and ethylene polymer resins meeting the aforementioned criteria are beneficially prepared under conditions characteristic of Ziegler polymerization in the presence of a transition metal-containing catalyst and at least one cocatalyst or activator. The cocatalyst is selected from the group consisting of aluminum, boron, zinc, or magnesium compounds represented by the formulas $Al(R^3)_{3-a}X^1{}_a$, $B(R^3)_{3-a}X^1{}_a$, $MgR^3{}_2$, MgR^3X^1, $ZnR^3{}_2$ or mixtures thereof. In these formulas, each R^3 is independently a hydrocarbyl group, X^1 is a halogen and a is an integer of from zero to two. U.S. Patent No. 4,526,943 (Fuentes Jr., et al) discloses such a process.

The transition metal-containing catalyst is suitably prepared in accordance with U.S. Patent Number 4,456,547 (Fuentes, Jr.). The catalyst results from admixing at least one each of four components in an inert hydrocarbon diluent and in an atmosphere which excludes moisture and oxygen. One component is a hydrocarbon-soluble organomagnesium material such as butylethylmagnesium. A second component is an organic alcoholic hydroxyl-containing material such as n-propyl alcohol. A third component is a reducing halide source

such as ethylaluminum dichloride. A fourth component is a transition metal-containing reaction product. The reaction product is formed by mixing, at a temperature and for a time sufficient to cause a desired color change, (1) at least one transition metal (Tm) compound and (2) at least one organozinc compound. The Tm compound has at least one hydrocarbyloxy group attached to the transition metal. The four components are added in the order stated except that addition of the third and fourth components can be reversed without adverse effects. The components are present in amounts sufficient to provide atomic ratios as follow: (a) Mg:Tm of 0.1:1 to 100:1; (b)Zn:Tm of 0.05:1 to 10:1; (c) Cl:Mg of 2:1 to 20:1; and (d) OH:total number of hydrocarbyl groups attached to the magnesium atom of the organomagnesium material of 0.5:1 to 1.5:1.

The transition metal-containing catalyst may also be prepared by admixing at least one each of four components in an inert hydrocarbon diluent and in an atmosphere which excludes moisture and oxygen. One component is a hydrocarbon-soluble organomagnesium material represented by the formula $R_2Mg.xMR'_{x'}$. In the formula each R is independently a hydrocarbyl group having from 1 to 20 carbon atoms; each R' is independently hydrogen or a hydrocarbyl group having from 1 to 20 carbon atoms; M is aluminum (Al) or zinc (Zn); x is an integer of from 0 to 10 and is sufficient to render the organomagnesium component hydrocarbon soluble; and x' has a value equal to the valence of M. The second and third components are suitably the same as those taught in U.S. Patent Number 4,456,547. The fourth component is represented by the formula TmY_nX_{z-n} or



In these formulas Tm is titanium in its highest stable valence state and Y is oxygen or OR". Each R is independently a hydrocarbyl group having from one to 20 carbon atoms and each R" is independently hydrogen or R. X is a halogen, z is an integer equal to the valence state of Tm, m is an integer of from one to 20 and n is an integer of from zero to four. The components are added in the order stated except that addition of the third and fourth components can be reversed without adverse effects. The components are present in amounts sufficient to provide atomic ratios as follows: (a)Mg:Tm of from 0.1:1 to 100:1, desirably from 1:1 to 40:1; (b) Cl:Mg of from 3:1 to 20:1, desirably from 6:1 to 20:1; and (c) OH: metal atom from the first component of from 2:1 to 3:1.

Other catalysts and processes may be used provided the polyethylene resins and ethylene polymer resins produced therewith meet the criteria specified herein.

The halogenated derivatives of polyethylene and ethylene polymers are suitably chlorinated derivatives. The chlorinated derivatives are respectively referred to herein as chlorinated polyethylene resins and chlorinated ethylene polymer resins.

The chlorinated polyethylene resins and chlorinated ethylene polymer resins have three distinctive physical properties. First, they have neat wedge blocking value of from 0 to 60 kilograms. The neat wedge blocking value is beneficially from 0 to 50 kilograms and desirably from 0 to 35 kilograms. Second, they have a weight-based median particle size of from 200 to 900 microns. The median particle size is beneficially from 200 to 700 microns and desirably from 200 to 500 microns. Third, they have a particular chemically combined halogen, preferably chlorine, content. The chlorinated polyethylene resins have a chlorine content which is suitably from 26 to 42, beneficially from 28 to 40, and desirably from 30 to 38 percent by weight of derivative. The chlorinated ethylene polymer resins have a chemically combined chlorine content which is suitably from 15 to 28 and beneficially from 19 to 26 percent by weight. It has been found that at chlorine contents of greater than 28 percent by weight, blocking of chlorinated ethylene polymer resins becomes excessive.

The chlorinated polyethylene resins and chlorinated ethylene polymer resins are prepared by chlorination of the polyethylene resins described herein. Chlorination may be accomplished by any known procedure provided the chlorinated derivatives have the aforementioned distinctive physical properties. In other words, chlorination may be accomplished by suspension, slurry and bulk, or fluidized bed, procedures. Suspension chlorination, for example, is disclosed in U.S. Patent 3,454,544.

The chlorinated polyethylene resins of the present invention may be used in any application where chlorinated polyethylene is conventionally used. One such application is as an impact modifier for polyvinyl chloride resins.

The following examples are only for purposes of illustration and are not to be viewed as limiting the present invention. All parts and percentages are on a weight basis unless otherwise stated. Examples of the present invention are represented by Arabic numerals whereas comparative examples not part of the present invention are represented by alphabetic characters.

Test Procedures

A. Sieve Analysis

Test sieves having a diameter of 8 inches (3.15 centimeters) and meeting American Society for Testing and Materials (ASTM) Test E-11 specifications were used for particle size analysis. The test sieves were available from W. S. Tyler Incorporated. Each test sieve had a different mesh opening. The test sieves were stacked in descending order with the sieve having the largest mesh or screen opening being at the top. A pan was placed under the lower test sieve and a cover was placed over the top test sieve to form a test sieve assembly.

In operation, the cover was removed and a one hundred gram resin sample was placed on the screen of the top test sieve. The cover was then replaced and the test sieve assembly was secured on a sieve shaker. The sieve shaker, commercially available from Arthur H. Thomas Company, was connected to a timer. The rate of

agitation of the sieve shaker was set on a rheostat scale which ranged from a setting of zero to a setting of one hundred. The resin sample was shaken for a period of 15 minutes at a rheostat scale setting of from 80 to 100.

After the fifteen minute period, the sieve shaker was stopped. Each of the test sieves was weighed first with and then without resin trapped thereon to determine sieve content weight. Weighing was done with a laboratory balance sensitive to 0.1 gram. Percentage of resin retained on screen was determined by the following formula:

$$\%\ \text{Retained} = \frac{\text{sieve content weight} \times 100}{\text{resin sample weight}}$$

B. Wedge Blocking Test

The wedge blocking test used herein is disclosed in U.S. Patent Number 4,412,448 (Flynn, et al). The test comprises two steps. In one step, a sample of particulate polymer resin is compressed between substantially parallel surfaces in a circular mold at a temperature of 50° Centigrade and a compression pressure of 515 Kilopascals (kPa) gauge for a period of three hours to form a test cake. The mold is then cooled to a temperature of 25°C and the test cake is removed therefrom. In a second step, an elongated, triangular-shaped wedge is forced into the cake at a constant rate of speed until the cake breaks. The force required to break the cake is known as the blocking value. The wedge has a sharp v-shaped configuration at an angle

of 60° which extends to the opposite edges of the test cake. An Instron tester described in ASTM Test D638-(1979) is used to force the wedge into the test cake.

The wedge blocking test was used to evaluate resins with and without inorganic particulate antiblock additives in admixture therewith.

Example 1 and Comparative Examples A-E

A. Identification of Polyethylene Starting Materials

Polyethylene resins, their source and their commercial designation, where applicable, are set forth in Table I. Each of these resins was subjected to Sieve Analysis as detailed herein. Results of the Sieve Analysis in terms of percent retained on each sieve are set forth together with sieve mesh opening in Table II. Weight based median particle size and two different particle size distributions are shown in Table III.

TABLE I Polyethylene Resins

Example/ Comparative Example	Source
1	A non-commercial high density polyethylene resin having a bulk density of 0.39 grams per cubic centimeter and a nominal melt index of 0.3 decigrams per minute. The resin was prepared by The Dow Chemical Company.
2	A non-commercial high density polyethylene resin having a bulk density of 0.42 grams per cubic centimeter

TABLE I Continued

Example/ Comparative Example	Source
	and a nominal melt index of 0.2 decigrams per minute. The resin was prepared by The Dow Chemical Company.
A	A high density polyethylene resin having a bulk density of 0.25 grams per cubic centimeter. The resin was commercially available from Arco Chemical Company under the trade designation SDP 640.
B	A high density polyethylene resin having a bulk density of 0.31 grams per cubic centimeter. The resin was commercially available from Arco Chemical Company under the trade designation SDP 113.
C	A high density polyethylene resin having a bulk density of 0.27 grams per cubic centimeter. The resin was commercially available from U. S. Industrial Chemicals Company under the trade designation FA 750.
D	A high density polyethylene resin having a bulk density of 0.45 grams per cubic centimeter. The resin was commercially available from American Hoechst Corporation under the trade designation GC 7260.
E	A high density polyethylene resin having a bulk density of 0.52 grams per cubic centimeter. The resin was commercially available from Allied Chemical Corporation under the trade designation 60-007.

TABLE II Polyethylene Sieve Analysis

Sieve Number	Screen Opening (Microns)	Percent of Resin Returned on Screen 1	2	A	B	C	D	E
20	850	0.7	0.3	0.1	0.1	0.1	0.5	14.9
30	600	6.4	0.6	0.3	0.5	0.1	0.7	32.8
35	500	16.1	1.1	0.7	0.2	0.2	0.7	14.0
40	425	22.0	2.0	1.6	0.8	0.1	0.6	12.5
45	355	21.9	3.6	2.7	5.7	0.2	1.3	9.1
50	300	12.7	8.2	0.3	3.3	0.7	2.9	6.8
60	250	8.7	12.1	0.2	1.8	0.9	6.2	2.7
70	210	3.4	18.6	0.5	2.2	1.3	17.5	3.2
80	190	2.9	12.5	0.5	10.3	1.6	13.5	1.0
100	150	1.5	15.0	10.8	2.3	2.0	19.0	1.3
pan	none	3.7	26.1	82.2	72.8	92.8	37.0	1.5

TABLE III Polyethylene Particle Size Data

Sample Identification	Median Particle Size (Microns)	Distribution (Percent) 150-850 microns	150-500 microns
1	410	96.3	89.2
2	178	73.9	73.0
A	l.t. 150	17.8	17.4
B	l.t. 150	27.2	6.6
C	l.t. 150	7.2	7.0
D	150	63.0	61.8
E	586	98.5	50.8

l.t. = less than

B. Chlorination of Polyethylene Resins

Each of the polyethylene resins listed in Table I was chlorinated by an aqueous slurry process in an enclosed versel. Each resin was slurried with about nine times its weight of water in an enclosed vessel. Gaseous chlorine was introduced into the slurry at a rate of 0.2 kilograms of chlorine per kilogram of polyethylene per hour. Chlorination began at a slurry temperature of 98° Centigrade. The slurry temperature was then slowly increased over a period of fourteen minutes to a temperature of 110° Centigrade. The chlorinated polyethylene had a chemically combined chlorine content of eight percent by weight of polymer after the fourteen minute period. The temperature of the slurry was then slowly increased over a period of 95 minutes to a temperature of 131° Centigrade. After the 95 minute period the chlorinated polymer had a chemically combined chlorine content of 36 percent by weight of polymer. Chlorination was then terminated and the slurry was filtered to remove the chlorinated polyethylene. The chlorinated polyethylene was washed and then dried at a temperature of 60° Centigrade for a period of 24 hours.

C. Wedge Blocking Test Results

Following chlorination of each of the polyethylene starting materials, wedge blocking test cakes were prepared using the procedure described herein. Some of the chlorinated materials were blended with an amount of an antiblock additive prior to preparation of the test cakes. The antiblock additive (hereinafter abbreviated as "AB") was calcium carbonate. The calcium carbonate was commercially available from

Pfizer under the trade designation Superflex™ 200. The test cakes were then subjected to the wedge blocking test described herein. The amount of calcium carbonate together with wedge blocking test force measurements are shown in Table IV.

Table IV - Wedge Blocking Test Results

Example/ Sample	Blocking Value (kilograms)+ Neat*	2% AB**	4% AB**
1	13.6	-	5.0
1	9.6	-	3.6
2	15.3	-	-
A	g.t. 113.6	g.t. 113.6	23.2
A	g.t. 113.6	59.1	37.7
A	g.t. 113.6	g.t. 113.6	99.1
A	g.t. 113.6	g.t. 113.6	g.t. 113.6
B	g.t. 113.6	54.1	19.6
B	g.t. 113.6	g.t. 113.6	g.t. 113.6
B	g.t. 113.6	g.t. 113.6	81.8
C	g.t. 113.6	g.t. 113.6	36.4
D	g.t. 113.6	g.t. 113.6	g.t. 113.6
D	104.6	30.9	15.9
E	70.4	51.8	25.0

+ Upper limit of test measurement was 113.6 Kilograms (250 pounds)

* No calcium carbonate admixed with chlorinated resin prior to forming test cake.

** Percent by weight of calcium carbonate admixed with chlorinated resin prior to forming test cake.

\- Test not run.

g.t. greater than

Table V -Chlorinated Polyethylene Sieve Analysis

Sieve Number	Screen Opening (Microns)	Percent of Chlorinated Resin Retained on Screen 1	2[a]	A[b]	B[c]	C	D[d]	E
20	850	0.9	0.1	7.4	23.1	9.5	3.2	26.2
30	600	7.8	0.4	14.3	23.2	27.4	2.8	38.7
35	500	17.1	1.7	22.7	17.4	33.7	1.7	10.8
40	425	23.4	7.3	22.9	12.5	21.7	3.2	11.1
45	355	19.7	17.7	19.1	8.6	5.1	7.6	5.6
50	300	12.6	24.7	10.3	5.4	1.9	14.0	2.5
60	250	8.3	18.0	2.5	4.9	0.3	28.2	2.0
70	210	2.0	17.6	0.6	2.6	0.1	16.3	1.4
80	190	4.4	5.2	0.1	1.3	0.0	10.3	0.7
100	150	1.9	4.5	0.0	0.8	0.0	7.9	0.7
pan	none	1.5	2.9	0.1	0.2	0.2	4.8	0.3
weight-based median particle size (microns)		422	254	481	579	561	225	696

a Average of 4 sieve analyses
b Average of 5 sieve analyses
c Average of 6 sieve analyses
d Average of 3 sieve analyses

A review of the data presented in Tables I - V highlights several points. First, the halogenated derivatives of the present invention (Samples 1 and 2) are less susceptible to blocking or agglomeration than halogenated derivatives of conventional polyethylene resins (Samples A-E). Second, the derivatives of the present invention differ physically from derivatives of conventional polyethylene resins in terms of both particle size distribution and weight-based median particle size (<u>See</u> Table V). Third, the derivatives of the present invention have a particle size growth, based on polyethylene

resin starting material, which is less than that of all comparative samples save Samples D & E (See, Tables II, III, and V). Similar results are obtained with other halogenated derivatives within the scope of the present invention.

Effect of Chlorine Content of Chlorinated Ethylene Polymer Upon Blocking

Samples of an ethylene polymer prepared by The Dow Chemical Company were chlorinated as described herein to different chlorine contents to determine the effect of chlorine content upon blocking. The ethylene polymer had polymerized therein 98.2 weight percent ethylene and 1.8 weight percent 1-butene, both percentages being based upon polymer weight. The ethylene polymer had a nominal melt index of 1.1 decigrams per minute and a density of from 0.948 grams per cubic centimeter. Following chlorination, wedge blocking test cakes were prepared using the procedure described herein. The test cakes were then subjected to the wedge blocking test described herein. Results of the wedge blocking test are presented in Table VI together with chlorine content and heat of fusion.

TABLE VI - Chlorinated Ethylene Polymer Wedge Blocking Test Results

Sample	Chlorine Content(%)	Heat of Fusion (Calories per gram)	Neat Wedge Blocking Value (kilograms)
3	21.4	1.13	7.7
4	23.7	2.59	11.9
5	26.2	0.09	10.9
F	28.2	1.09	71.6

A review of the data presented in Table VI demonstrates that as chlorine content increases beyond 28 percent by weight of polymer, blocking becomes unacceptably high. Similar results are obtained with other halogenated ethylene polymers which are representative of the present invention.

1. An agglomeration-resistant, halogenated derivative of polyethylene, characterized by (a) having (1) a neat wedge blocking value of from 0 to 60 kilograms, (2) a weight-based median particle size of from 200 to 900 microns and (3) a chemically combined halogen content of from 26 to 42 percent by weight of derivative; and (b) being prepared from a polyethylene resin having (1) a weight-based median particle size of from 160 to 600 microns, (2) a weight-based particle size distribution such that more than 60 percent of the particles have a particle size of from 150 to 850 microns, (3) a bulk density of from 0.26 to 0.56 grams per cubic centimeter and (4) a density of from 0.958 to 0.965 grams per cubic centimeter.

2. The halogenated polyethylene of Claim 1 wherein the halogen is chlorine.

3. The halogenated polyethylene of Claim 1 wherein the polyethylene resin has a weight-based median particle size of from 160 to 450 microns.

4. The halogenated polyethylene of Claim 1 wherein the polyethylene resin has a weight-based particle size distribution such that more than 60 percent of the particles have a particle size of from 150 to 500 microns.

5. The halogenated polyethylene of Claim 1 wherein the neat wedge blocking value is from 0 to 50 kilograms.

6. The halogenated polyethylene of Claim 1 wherein the derivative has a weight-based median particle size of from about 200 to about 500 microns.

7. The halogenated polyethylene of Claim 2 wherein the chlorine content is from about 28 to about 40 percent by weight of derivative.

8. An agglomeration - resistant, halogenated derivative of an ethylene polymer, the ethylene polymer having polymerized therein, on a polymer weight basis, from 95 to 99 percent ethylene and from 5 to 1 weight percent of 1-olefin monomer copolymerizable therewith, characterized in that said halogenated derivative has (a) a chemically combined halogen content of from 15 to 28 percent by weight of derivative, (b) a weight-based median particle size of from 200 to 900 microns, (c) a neat wedge blocking value of from 0 to 60 kilograms and (d) a heat of fusion of from 0 to 3 calories per gram and being prepared from said ethylene polymer having (a) a weight-based median particle size of from 160 to 600 microns, (b) a particle size distribution such that, on a weight basis, more than 60 percent of the particles have a particle size of 150 to 850 microns and (c) a bulk density of from 0.26 to 0.56 grams per cubic centimeter.

9. The halogenated ethylene polymer of Claim 8 wherein the halogen is chlorine.

10. The halogenated ethylene polymer of Claim 8 wherein the derivative has a weight-based median particle size of from 200 to 500 microns.

11. The halogenated ethylene polymer of Claim 8 wherein the ethylene polymer resin has a weight-based particle size distribution such that more than 60 percent by weight of the particles have a size of from 150 to 500 microns.

12. The halogenated ethylene polymer of Claim 9 wherein the chlorine content is from 19 to 26 percent by weight of polymer.

13. The halogenated ethylene polymer of Claim 8 wherein the ethylene polymer has a density of from 0.935 to 0.950 grams per cubic centimeter.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/02329

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [8]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 08 F 8/20

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 08 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 4029862 (G.Y.T. LIV) 14 June 1977, see claims 1,2; column 2, line 25 - column 3, line 54	1-13
Y	FR, A, 2381069 (STAMICARBON) 15 September 1978, see claims 1-16	1-13
Y	US, A, 4456547 (R. FUENTES Jr.) 26 June 1984, see claims 1-4 (cited in the application)	1-13
A	GB, A, 922678 (HOECHST) 3 April 1963, see claim 1	1
A	GB, A, 1167460 (ALLIED CHEMICAL) 15 October 1969, see claim 1	1

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* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
24th March 1986	17 AVR. 1986
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 85/02329 (SA 11595)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 09/04/86

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4029862	14/06/77	None		
FR-A- 2381069	15/09/78	NL-A-	7701599	18/08/78
		BE-A-	863924	14/08/78
		DE-A-	2806653	17/08/78
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GB-A- 1167460	15/10/69	None		

For more details about this annex :
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